

Fig. 1. Average catalytic efficiency of the ligases in the test protocell over the course of a simulation. The solid line represents the results of a reference model, in which the probability of forming an efficient ligase was slightly less than the probability of forming an efficient protease; there was a strong preference for the hydrolysis of unstructured peptides. The dashed line displays the results of a simulation in which the probability of forming an efficient ligase has been lowered.

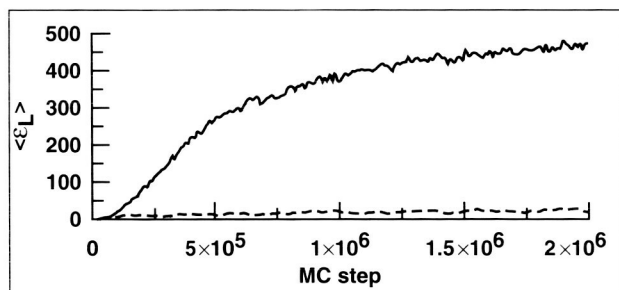


Fig. 2. Average catalytic efficiency of the ligases in the test protocell over the course of a simulation. The solid line displays the same reference model as in figure 1. The dashed line displays the results of a simulation in which the preference for the hydrolysis of unstructured peptides has been reduced slightly.

peptides is reduced slightly (dashed line) relative to the reference model (solid line). When efficient proteases are easy to form, or when there is little preference for the hydrolysis of unstructured peptides, any long and highly efficient peptides will be destroyed before they can greatly affect the population of peptides within the protocell. Therefore, the rate at which the protocell generates new, and possibly efficient, peptides will be slow.

The results presented here demonstrate the possibility of a novel mechanism of early

protocellular evolution. This mechanism does not require the presence of a genome, nor does it rely on any form of sequence complementarity or the exact replication of proteins. It is the preservation of cellular functions and their interrelationships that must be maintained during this early stage of evolution, not the identity of the actors performing those functions.

**Point of Contact:** M. New  
(650) 604-4762  
mnew@mail.arc.nasa.gov

## Reduced Nitrogen for an Acidic Early Ocean

David P. Summers

This project studies how reduced nitrogen (nitrogen with a low oxidation state) may have been available for the origin of life on the Earth (and potentially on other planets such as Mars). Life today uses nitrogen in a relatively reduced state. Organisms produce that nitrogen biochemically. However, at the time of the origin of life, those biochemical mechanisms were not yet in place. Therefore, there must have been a nonbiological mechanism to produce such nitrogen. Without the availability of reduced nitrogen for the formation of species such as amino and nucleic acids, life could not have started.

One important form of fixed and reduced nitrogen is ammonia. However, current geochemical evidence points to an atmosphere on the early Earth that contained elemental nitrogen ( $N_2$ ) instead of ammonia. The lighting that would have produced, ultimately, amino acids under a methane/ammonia atmosphere produced only nitrogen monoxide (NO). However, this NO can be converted into nitrite ( $NO_2^-$ ) and nitrate ( $NO_3^-$ ) by atmospheric and aqueous processes. Work at Ames has previously shown that one source of ammonia involves the reduction of nitrite to ammonia by the aqueous ferrous iron (iron in the +2 oxidation state; in this case the  $Fe^{+2}$  ion), which was common on the early Earth. However, this reaction doesn't form ammonia

at acidic pHs (<7.3). The early Earth is thought to have had a carbon dioxide atmosphere, and since carbon dioxide is acidic, an acidic early ocean is a distinct possibility.

This work has found that a form of ferrous iron, FeS (one form of iron sulfide), will reduce nitrite and nitrate to ammonia under acidic conditions. With regard to nitrite ( $\text{NO}_2^-$ ), figure 1 shows how the concentration of ammonium changes with time when nitrite is added to a suspension of FeS under acidic conditions (pH 6.3). Ammonia is formed at pH 6.3 and, in fact, at all pHs studied. As the pH becomes more acidic, the yield of ammonia (the amount of nitrite that is converted to ammonia) increases from 18% to 53%. This increase is thought to be due to the fact that, under carbon dioxide, less bicarbonate (an ion that is a neutralized form of carbon dioxide) is present in more acidic solutions, and bicarbonate interferes with the reactions. Similarly, it was found that there is a small, but noticeable, decrease in the yield of ammonia when chloride and sulfate ions are added. Presumably these ions tend to block the surface of the FeS particles, preventing the nitrite ion from getting in to react. A phosphate ion has an even bigger effect, cutting the yield by two-thirds.

FeS also reduces nitrate ( $\text{NO}_3^-$ ) under acidic conditions. Yields from nitrate are much lower, typically 7% in a more acid solution (pH <5), and no ammonia is formed at any neutral pHs. Similarly, the reduction of nitrate is much more sensitive to the presence of added species. No ammonia was produced in the presence of chloride, sulfate, or phosphate ions. It appears as if nitrate is much more sensitive to the presence of blocking ions. Perhaps nitrate is more easily blocked from the surface. The reduction of nitrate was observed with  $\text{Fe}^{+2}$ , but the reaction was never found to be reproducible (different yields were obtained when the reaction was run under what apparently were the same conditions). The lack of reproducibility of nitrate reduction by  $\text{Fe}^{+2}$  (which also showed a similar effect) might be related to the ease with which the reaction is poisoned.

After reactions, analysis of the surface composition by a scanning electron microscope with a light element detector did not indicate the formation of any iron oxide (see figure 2). However, iron was found dissolved in the solution. Thus, oxidation of the FeS during the reduction of nitrite proceeds by

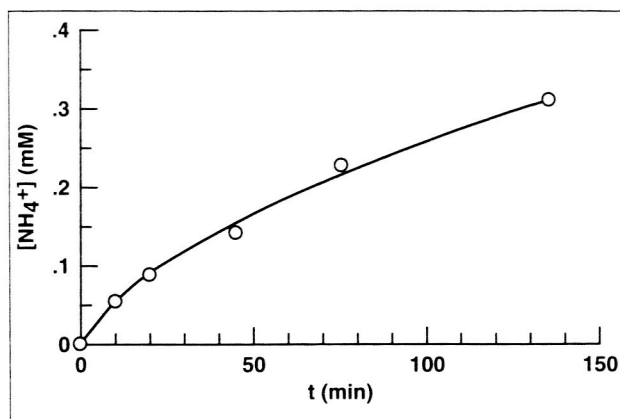


Fig. 1. Ammonium concentration versus time in the reduction of nitrite by FeS under carbon dioxide at pH 6.3.

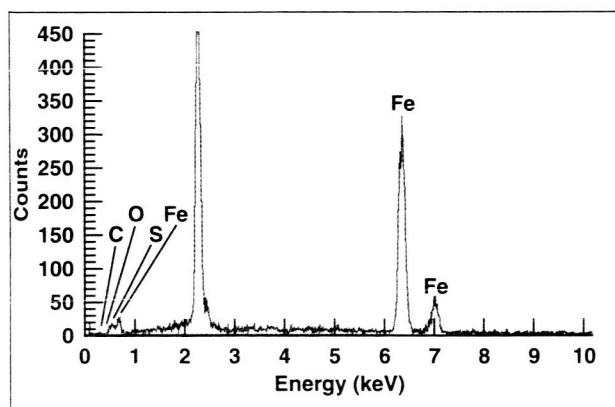


Fig. 2. Surface composition of a particle of FeS after reaction with nitrite.

the formation of  $\text{FeS}_2$  at the surface and  $\text{Fe}^{+3}$  in solution.

Clearly, FeS is a good reductant for the conversion of nitrite and nitrate to ammonia. The reaction occurs under acidic conditions, meaning that such reduction would have been a viable source of ammonia, even if the early oceans were acidic. The reduction of nitrite tolerates the presence of many of the salts that would likely have been present in an early ocean, though some drop in yield is seen. The reduction of nitrate is more sensitive.

**Point of Contact: D. Summers**  
(650) 604-6206  
dsummers@mail.arc.nasa.gov